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Technical Report No. 4
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Errata

TECHNICAL REPORT NO. 4

Presented to

The Office of Naval Research

Project Number NR 057-233

Contract Nonr-03700

under the direction of Edward S. Amis

entitled

THE DIELECTRIC CONSTANT AND SALT EFFECTS UPON THE ACID HYDROLYSIS OF ETHYL FORMATE

by

Navin P. Shah and Edward S. Amis

University of Arkansas

Department of Chemistry

November 26, 1952

Errata dated January 27, 1953

Page 2, 3rd line from bottom-Insert "at 720 mm. pressure" after 56.0° C.

Page 15 should follow page 12. The material on page 15 is a continuation of that on page 12.

The last sentence in the paragraph immediately following equation (8) on page 12 should read: "Thus from the standpoint of coulombic energies it is possible to accept the ion-dipole molecule mechanism for the acid hydrolysis of ethyl formate.

The enclosed Table III showing the activation energy values from which $\Delta E_{c(obs)}$ were obtained should be inserted instead of Table III which appears in the report. The activation energy values in the latter table have been rounded and do not show these differences.

Table III

Experimental and Calculated Values of Energies of Activation for Solvent Effect

Ionic Strength: 0.0200 HCl: 0.0200M Ethyl formate: 0.0100M

Between Temperatures : 35.01° C and 45.11° C.

D	$k' \times 10^3$ min^{-1} @ 35.01° C	$k' \times 10^3$ min^{-1} @ 45.11° C	$\Delta E_{(obs)}$	$\Delta E_{c(obs)}$	$\Delta E_{c(cal)}$
66.68	4.62	13.9	21,590		
62.44	4.06	12.5	21,680	90	78.9
58.88	3.66	11.1	21,790	110	75.0
55.59	3.30	10.3	21,910	120	78.0

Between Temperatures : 45.11° C and 55.02° C

	@ 45.11° C	@ 55.02° C			
66.68	13.9	40.9	22,150		
62.44	12.5	37.0	22,150	0	78.9
58.88	11.1	33.5	22,180	30	75.0
55.59	10.3	30.5	22,210	30	78.0

Between Temperatures: 35.01° C and 55.02° C

	@ 35.01° C.	@55.02° C.			
66.68	4.62	41.0	22,990		
62.44	4.06	37.0	22,140	50	78.9
58.88	3.66	33.5	22,210	70	78.0
55.59	3.30	30.5	22,280	70	78.0

Experimental Values of Frequency Factor for Solvent Effect

Ionic Strength: 0.0200 HCl:0.0200 M Ethyl Formate:0.0100M
Dielectric Constant:62.44

Temperature °C	Frequency Factor
35.01 - 45.11	10.07×10^{12}
45.11 - 55.02	12.88×10^{12}

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by

Navin P. Shah and Edward S. Amis

UNIVERSITY OF ARKANSAS

Department of Chemistry

November 28, 1952

Fayetteville, Arkansas

THE DIELECTRIC CONSTANT AND SALT EFFECTS UPON THE ACID HYDROLYSIS OF ETHYL FORMATE

By

Navin P. Shah and Edward S. Amis

ABSTRACT

The hydrolysis of ethyl formate catalyzed by hydrochloric acid was studied at three temperatures in water-acetone media and in water media containing different concentrations of sodium nitrate. The effect of various ionic strengths and dielectric constants upon the rate of acid hydrolysis of ethyl formate is presented from the stand point of electrostatics and the results were compared to like effects upon the acid hydrolysis of ethyl acetate and methyl propionate. Neither the dielectric constant effect nor the salt effect lends itself readily to theoretical interpretation. It was assumed that a partial explanation of these anomalous results might be in the extrapolation of the acid radical to the simplest carboxylic acid. This suggestion was supported somewhat by the trends towards less adherance to the electrostatic theory at certain temperatures in the series methyl propionate, ethyl acetate and ethyl formate.

It was thought that the study of both the acid and basic hydrolysis of esters as a function of the dielectric constant of the solvent and of neutral salt concentration would be of interest in view of existing theories of rates of reactions between ions and dipolar molecules. Since esters are hydrolyzed by both

hydronium and hydroxyl ions the theories of ion-dipolar reaction rates could be investigated with respect to both positive and negative ions reacting with an identical dipolar molecule under like conditions of concentrations of reactants, temperature, and dielectric constant of solvent.

Experimental

The C. P. Ethyl Formate, Eastman Kodak is manufactured in a high state of purity and therefore the reagent was simply dried over burnt lime for 24 hours and then distilled at an atmospheric pressure of 725.5 mm of mercury. The fraction coming off between 52.1-52.2° C was collected. The density of ethyl formate was measured at 27° C and was found to be 0.89511 g/ml. Ethyl formate used in all kinetic runs was kept at 27° C and the required quantity of pure ethyl formate (0.4140 ml) was added to the reaction solution at various temperatures. It was assumed that a negligible drop in the temperature of the reaction occured.

The acetone was prepared according to the procedure of Akerlof(1) as follows: Acetone, J. T. Baker analyzed, was treated in batches of about three liters with a small amount of 85% bone phosphoric acid and immediately distilled. Then it was dried with burnt powdered lime for a day, poured off and redistilled; the fraction which came over between 55.5 and 56.0° C was collected. Weight percent of acetone for a kinetic run was calculated from the density determination of acetone at various temperatures.

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(1) Akerlof, G., J. Am. Chem. Soc., 54, 4125 (1928).

Sodium nitrate, J. T. Baker analyzed; c.p. was used to prepare 1.0000 N $NaNO_3$ stock solution; and this concentrated solution was then diluted to the required normality for various kinetic runs on salt effect.

Freshly boiled distilled water was always used in preparing solutions. A carbonate-free concentrated sodium hydroxide stock solution (about 0.4 N) was prepared. The concentrated solution was then diluted in batches and standardized against potassium biphthalate and stored in a paraffin-lined carboy. From this stock solution was prepared 0.0100 N solution actually used in the kinetic runs.

A 0.4857 N HCl stock solution was prepared by diluting c.p. concentrated (37%) acid and titrating against sodium carbonate. Then the 0.0200 N HCl used in the runs was prepared as needed by dilution of the stock solution.

All volumetric apparatus and a set of analytical weights were calibrated and Bureau of Standard thermometers were used. The rate of hydrolysis was studied at temperatures of 35.01, 45.11 and 55.02° C. Insulated distilled water baths equipped with efficient stirring motors controlled the temperature within ±0.01° C of the desired temperature.

Analytical techniques were checked by duplicating a kinetic run whose reaction velocity constant has been established. The acid hydrolysis of ethyl acetate as reported by Harned and Pfanstiel(2)

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(2) Harned, H. S., and Pfanstiel, R., J. Am. Chem. Soc., 44, 2193 (1922).

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was selected for this purpose. Exact duplication of their experi-

mental work gave very good checks of their reported velocity constants. This indicated that both the reagents and technique were satisfactory. No experimental results were available concerning the acid hydrolysis of ethyl formate.

The procedure to determine the kinetics of the acid hydrolysis of ethyl formate under conditions of varying (1) ionic strength, and (2) dielectric constant was as follows: Flasks containing the reagents were immersed in the thermostat and left for four hours for attainment of temperature equilibrium. Reaction was carried out in a calibrated volumetric flask. Concentrated solutions of reagents were prepared so that mixing them in the reaction flask and bringing the mixture to the volumetric mark by the addition of distilled water gave the desired concentration of each reagent. Duplicate runs were made in every case. The desired ionic strength was attained by adding the required amount of stock sodium nitrate solution. The addition of acetone in correct amounts gave the required dielectric constants for kinetic runs on the solvent effect. The reaction were followed by periodic withdrawals of 10.00 ml samples of the reacting mixture. The contents of the pipette were allowed to drain upon crushed ice prepared from distilled water to stop further hydrolysis of the ester. When the pipette was half empty the time was recorded. The cold samples, approximately 0.2° C, were then titrated with 0.0100 N sodium hydroxide to a phenol-phthalein end point. The reactions were followed until hydrolysis was approximately 70% complete when possible. A final titration was made after the reaction had ample time to reach completion usually several hours.

The reaction velocity constant, k', was calculated using the

first-order equation

$$dx/dt = k\ (A-x) \qquad (1)$$

where dx/dt is the velocity of reaction,

A represents the initial concentration of ester

x the amount of ester changed in time t

k' the velocity constants of hydrolysis.

integrating equation (1)

$$k' = 1/t \ln A/(A-x) \qquad (2)$$

Equation (2) expressed in terms of the number of milliliters of alkali employed in the titration becomes

$$k' = \frac{2.303}{t} \log (T_\infty - T_0) / (T_\infty - T) \qquad (3)$$

where T_∞ = Theoretical number of ml of alkali required for complete hydrolysis

T_0 = Initial titration, ml. of alkali

T = Titration value at time t; ml. of alkali

t = Time in minutes

k' = specific velocity constant, min^{-1}.

It can be seen from equation (3) that a plot of log $(T_\infty - T_0)/(T_\infty - T)$ against t should give a straight line, and the specific velocity constant, k', can be calculated from the slope of the straight line. This was the method used in calculating most of the k' values. In some instances k' values were obtained by inserting titration and time values in equation (3).

The precision of the titrations and the agreement of the two methods of calculating k' are shown by the typical data in Table I.

Table I

Dielectric Data

Bath Temperature 55.00 ± 0.02° C.
Solvent 16.80% Acetone by Weight

Ethyl Formate 0.0100 M
HCl 0.0200 M
NaOH 0.009627 M

Time (Min)	NaOH (Ml)	$T_\infty - T$	log $T_\infty - T$	$k' \times 10^2$ (Min$^-$)
0	20.75	10.39	1.0165	.
9	23.60	7.54	0.8774	3.56
17	25.30	5.84	0.7664	3.39
24	26.30	4.84	0.6848	3.18
29	27.25	3.89	0.5899	3.39
38	28.30	2.84	0.4533	3.50
44	28.60	2.54	0.4048	3.20
50	29.20	1.94	0.2878	3.36
59	29.70	1.44	0.1584	3.35
68	30.10	1.04	0.0170	3.39
75	30.30	0.84	T.9243	3.35
∞	31.14			
			Average	3.36
			Graphical Result	3.40

Dielectric Constant Effect

In Table II are recorded the kinetic data at constant acid and ester concentration and constant ionic strength. In these data the dielectric constant decreases with increasing weight per cent acetone component of solvent. In addition to the specific velocity constant, k' the energies of activation and the Arrhenius frequency factors are included in Table II. The energies were calculated from the k'/C_{H_2O} values using the integrated Arrhenius equation which may be stated

$$\ln \frac{k'_2/(C_{H_2O})_2}{k'_1/(C_{H_2O})_1} = \frac{\Delta E}{R} \quad \frac{(T_2-T_1)}{T_2\ T_1} \tag{4}$$

The frequency factor, B, was calculated using k'/C_{H_2O} values from an equation

$$B = \frac{T_2 \log (k'_2/(C_{H_2O})_2) - T_1 \log (k'/(C_{H_2O})_1)}{T_2 - T_1} \tag{5}$$

In general the ΔE and B quantities decrease with decreasing dielectric constant through a minimum and then increase continuously. The numerical value of these quantities are those observed in many instances for reactions in solutions.

In Figure 1 is plotted log k' versus percent acetone by weight for the three temperatures, 35.01, 45.11 and 55.02° C. The specific velocity constant, k' decrease with increasing concentration of acetone in a linear manner for all three temperatures except for the solutions containing higher percentages of acetone. The data at 55.02° C are observed to depart from linearity at a lower percentage of acetone than those at other temperatures.

Table II

Experimental Values of Velocity Constants as a Function of Dielectric constant; Corresponding Energies of Activation and Frequency Factors

Temperature 35.01° C.

Ionic Strength 0.0200 HCl 0.0200 M Ethyl Formate 0.0100 M

Acetone % by wt.	D	$k' \times 10^3$ min^{-1}	$\frac{k'}{C_{H_2O}} \times 10^5$ $Min^{-1}\ mol^{-1}$	ΔE (35.01-45.11) °C	B (35.01-45.11) °C
0.0	74.82	5.85	10.64	20,100	10.29
8.4	70.47	5.16	10.43	19,200	9.64
16.8	66.07	4.47	10.17	18,900	9.40
25.4	60.95	3.85	10.01	18,700	9.24
34.5	55.34	3.30	10.01	18.500	9.17
44.1	49.55	2.90	10.55	17,700	9.57
54.0	43.35	2.55	11.60	17,200	9.21
64.6	36.73	2.38	14.4	16,100	8.59
75.7	30.34	2.30	20.9	15,200	8.13

Temperature 45.11°C

				(45.11-55.02) °C	(45.11-55.02) °C
0.0	71.20	16.5	29.9	20,800	10.78
8.4	66.99	13.9	28.5	21,400	11.15
16.8	62.37	11.8	26.8	22,200	11.66
25.4	58.08	10.05	26.1	22,900	12.14
34.5	52.97	8.55	25.9	24,000	12.90
44.1	47.10	7.20	26.2	25,500	13.90
54.0	41.50	6.15	28.0	26,600	14.75
64.6	34.99	5.45	33.1	26,700	12.42
75.7	28.71	5.03	45.7	26,800	18.90

Table II (Cont'd)

Temperature 55.02° C

Acetone % by wt.	D	$k' \times 10^3$ min^{-1}	$k'/C_{H_2O} \times 10^5$ $min^{-1}\ mol^{-1}$
0.0	67.92	44.5	81.0
0.4	63.83	38.5	77.9
16.8	59.57	34.0	77.4
25.4	55.21	30.0	78.0
34.5	50.35	27.0	81.9
44.1	44.87	24.3	88.5
54.0	39.36	22.0	100.1
64.6	33.27	20.0	121.4
75.7	27.42	19.0	172.7

In figure 2 is plotted log of specific velocity constant, k' versus the reciprocal of the dielectric constant of the medium. The specific velocity constant, k' decreases with decreasing dielectric constant showing a linear relationship in the region of higher dielectric constant. A departure from linearity was observed for all three temperatures at dielectric constant values between 55.5 to 58.8. These curves were similar to those of Hockersmith and Amis (3) and Nair and Amis (4). The straight line portions of the

(3) Hockersmith, J. L. and Amis, E. S., Technical Report No. 2 to the Office of Naval Research, Project No. NR 057-233, Contract Nonr-03700, October 25, 1952. Presented to the J. Am. Chem. Soc., for consideration for publication.

(4) Nair, P. M. and Amis, E. S., Technical Report No. 3 to the Office of Naval Research, Project No. NR 057-233, Contract Nonr-03700, October 28, 1952. Presented to the J. Am. Chem. Soc., for consideration for publication.

curves gave r values of 4.25, 4.38 and 4.48. Angstroms at temperatures of 35.01, 45.11, 55.02 respectively. Thus values of r found are of molecular dimension; which should be the case since r is essentially the radius of the intermediate in the kinetic process. The calculation was made using the equation

$$S = - \frac{Z_A Z_B \epsilon^2}{2.303\, kTr} \qquad (6)$$

where S = The slope of the log k' vs 1/D plot,

Z_A, Z_B = valence of the ions; A and B respectively,

ϵ = electronic charge

k = Boltzman Constant

T = Absolute temperature

r = radius of the intermediate in the kinetic process

The magnitude and signs of the slopes of the curves and experimental values of r indicate the mechanism of the reaction involves a rate controlling step between ions of like signs. But it is not possible to accept this mechanism because no reasonable mechanism involving ions of like sign can be formulated for the acid hydrolysis of an ester and the reaction species, water, should not be ignored even though it was a component of the solvent.

In figure 3 is plotted log k'/C_{H_2O} against the reciprocal of dielectric constant of the medium for the three temperatures under investigation. Hockersmith and Amis (3) and Nair and Amis (4) plotted similar curves for the acid hydrolysis of methyl propionate and ethyl acetate respectively. The portions of their curves corresponding to higher value of dielectric constant were straight lines having magnitudes and signs of slopes indicating the controlling step in the reaction was one in which a positive ion reacted with a dipolar molecule. Hockersmith and Amis (3) accept the following mechanism for the acid hydrolysis of the esters:

$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R' + H_3O^+ \rightleftharpoons \left[R\text{-}\overset{\overset{OH_2^+}{|}}{\underset{\underset{OH}{|}}{C}}\text{-}O\text{-}R' \rightleftharpoons R\text{-}\overset{\overset{OH}{|}\,H}{\underset{\underset{OH}{|}\,+}{C}}\text{-}O\text{-}R' \right] \longrightarrow R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + R'OH + H^+ \quad (7)$$

They stipulate, however, that a step involving the product of the concentration of the positive ion and the concentration of dipole molecule governs the rate. No such conclusions can be drawn from the present data since log k'/c first decreased, passed through a minimum, and then increased as the reciprocal of dielectric constant of the medium increased at all three temperatures. The shapes of the curves are reminiscent of catalytic catenaries. This suggests that the main influence of the solvent in the acid hydrolysis of

ethyl formate is exerted upon the hydronium ion, and is effective by changing the activity of the ion.

Further calculations were made to confirm the ion-dipole mechanism from the energy standpoint. Coulombic energies arising from the change in dielectric constant of the medium were calculated from the equation (5)

(5) Amis, E. S., "Kinetics of Chemical Change in Solutions," The Macmillan Company, New York, 1949, p.77 and p. 182.

$$\Delta E_c = \frac{69.1 \; Z\mu}{D_1 D_2 r^2} \Delta D \qquad (8)$$

Where ΔE_c coulombic energy, ΔD was the difference between D_2 and D_1 and the other terms have their usual significance. These calculated values of coulombic energies together with observed values were recorded in Table III. In the calculation of these coulombic energies the same r value was used that was obtained from the log k' versus 1/D plots. The observed values of the coulombic energies differed by a reasonable magnitude from the calculated values. Thus it was not possible to accept the ion-dipole mechanism for the reaction of acid hydrolysis of ethyl formate.

The authors could find no electrostatic interpretation which was consistent with the data. However, the data for methyl propionate and ethyl acetate were explained on the basis of electrostatics. The dielectric constant data for acid hydrolysis of methyl propionate in acetone-water mixtures were well confirmed by electrostatic interpretation at all temperatures investigated. The data for ethyl acetate in acetone-water mixtures were progressively less amenable to electrostatics with increasing temperatures. Since data of ethyl acetate show some deviations from electrostatic requirements, extrapolation to the ester of formic acid might be expected

Table III

Experimental and Calculated Values of Energies of Activation for Solvent Effect

Ionic Strength: 0.0200 HCl: 0.0200M Ethyl Formate: 0.0100M

Between Temperatures; 35.01° C. and 45.11° C.

D	$k' \times 10^3$ min^{-1} @ 35.01° C	$k' \times 10^3$ min^{-1} @ 45.11°C	E_{obs}	ΔE_{obs}	$\Delta E_{Cal.}$
66.68	4.62	13.9	21,600		
62.44	4.06	12.5	21,700	190	78.9
58.88	3.66	11.1	21,800	110	75.0
55.59	3.30	10.3	21,900	120	78.0

Between Temperatures: 45.11° C. and 55.02° C.

	@ 45.11°C	@55.02° C.			
66.68	13.9	40.9	22,200		
62.44	12.5	37.0	22,200	0	78.9
58.88	11.1	33.5	22,200	30	75.0
55.59	10.3	30.5	22,200	30	78.0

Between Temperatures: 35.01° C and 55.02° C

	@35.01° C.	@55.02° C.			
66.68	4.62	41.0	22,100		
62.44	4.06	37.0	22,100	50	78.9
58.88	3.66	33.5	22,200	70	78.0
55.59	3.30	30.5	22,300	70	78.0

Experimental Values of Frequency Factor for Solvent Effect

Ionic Strength: 0.0200 HCl:0.0200 M Ethyl Formate: 0.0100M
Dielectric Constant:62.44

Temperature °C.	Frequency Factor
35.01 - 45.11	10.07×10^{12}
45.11 - 55.02	12.88×10^{12}

Salt Effect

In Table IV are recorded the kinetic data when the solvent was water and ionic strength was changed with increasing concentration of neutral salt ($NaNO_3$). In Figure 4 is plotted log k' against the negative logarithm of the activity of hydronium ion for three temperatures under investigation. The activity of hydronium ion was obtained by calculating activity coefficient-using the first approximation of Debye-Huckel theory and the distance of closest approach from Figure 2. The equation for this first approximation is

$$-\ln f_{H_3O^+} = \frac{2^2_{H_3O^+} A\sqrt{\mu}}{H B a_i \sqrt{\mu}} \qquad (9)$$

Where $f_{H_3O^+}$ is the activity coefficient of the hydronium ion of valence $Z_{H_3O^+}$ in a solution of ionic strength μ; A and B are the Debye-Huckel constants, which can be calculated from the known properties of the solvent and certain physical constants, and a_i is the distance of closest approach of two ions. Using the activity coefficients of hydronium ion and the concentrations of the hydrochloric acid, the activities of the hydronium ion in the various concentrations of reacting solutions could be found by multiplying the activity coefficient of the hydronium ion by its concentration. The concentration of the hydronium ion was assumed to be the same as the concentration of the acids-Hockersmith and Amis (3) found that plots of log k' against the negative logarithms of the activity of the hydronium ion for methyl propionate were catalytic catenaries of Class B as classified by R. P. Bell. (6)

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(6) Bell, R. P., "Acid-Base Catalysis", Oxford, the Clarendon Press, 1941, pp. 6-10 and 21-35.

to diverge from the required electrostatic interpretation when a common solvent (acetone-water, is used in all three cases. How to explain the continual shift away from the electrostatic interpretation as one goes from methyl propionate, to ethyl acetate, to ethyl formate is not clear unless specific solvent effect becomes progressively smaller. The decreasing size of the acid radical might be involved in the progressive departure of the data from the electrostatic theory, since in general, theoretical electrostatic relations are formulated to confirm data involving larger particles.

Table IV

Experimental Values of Velocity Constants as a Function of Ionic Strength: Corresponding Energies of Activation Frequency Factors, and Activity Coefficients

Temperature 35.01° C

D= 74.82 Total Ionic strength μ	; HCl: $k^1 \times 10^2$ min^{-1}	0.0200M $f_{H_3O^+}$	Ethyl Formate: 0.0100M ΔE (35.01-45.11) °C.	B (35.01-45.11) °C
0.0200	5.85	0.9556	20,100	12.03
0.0400	5.78	0.9133	20,100	12.03
0.0600	5.75	0.8976	20,000	12.00
0.0800	5.76	0.8853	20,000	11.95
0.1000	5.78	0.8752	19,900	11.92
0.1200	5.80	0.8664	19,900	12.03
0.1400	5.85	0.8586	19,900	11.90
0.1800	6.02	0.8453	19,700	11.78
0.2200	6.25	0.8341	19,400	11.57
0.2600	6.45	0.8243	19,300	11.50
0.3000	6.75	0.8166	18,900	11.25
0.3400	7.12	0.8087	18,500	11.00

Temperature 45.11°C

			(45.11-55.02) °C.	(45.11-55.02) °C.
0.0200	16.5	0.9396	20,800	12.41
0.0400	16.3	0.9206	19,900	11.85
0.0600	16.2	0.9080	19,500	11.50
0.0800	16.1	0.8984	19,300	11.33
0.1000	16.1	0.8908	19,100	11.20
0.1200	16.2	0.8843	19,000	11.17
0.1400	16.3	0.8784	19,000	11.19
0.1800	16.6	0.8691	19,500	11.53
0.2200	17.0	0.8611	20,700	12.34
0.2600	17.4	0.8549	22,200	13.36
0.3000	17.9	0.8494	23,800	14.50
0.3400	18.5	0.8445	25,400	15.60

Table IV (Cont'd)

Temperature 55.02°C.

Total Ionic strength (μ)	$k' \times 10^3$ min^{-1}	$f_{H_3O^+}$
0.0200	44.6	0.9383
0.0400	42.0	0.9356
0.0600	41.0	0.9063
0.0800	40.4	0.8969
0.1000	40.1	0.8888
0.1200	40.2	0.8820
0.1400	40.5	0.8764
0.1800	42.2	0.8668
0.2200	45.6	0.8570
0.2600	50.1	0.8525
0.3000	55.8	0.8468
0.3400	62.2	0.8419

In the class B catenaries the sides intersect at a sharp minimum with a slope of approximately 45 degrees with the horizontal. The catenaries obtain in the present investigation show a rounded minimum and sides rising steeply. The shapes of those catenaries are not similar to those of the ordinary classes of catenaries found in the literature. This could not be explained on electrostatic theory from the standpoint of primary salt effect (5) since if such was the case the positive-ion and neutral molecule mechanism should show an increase in the rate of reaction with increase in ionic strength. This is not the case as it could be seen from Figure 5 where log of the specific velocity constant was plotted against ionic strength at the three temperatures investigated. These plots showed an almost horizontal portion extending over half the ionic strength range before the rate constant increase was observed with increase in ionic strength.

Acknowledgment

The authors wish to acknowledge the help of Mrs. Ute-Reichhardt-Shah for assisting in calculating the data.

Fig. 1 - Solvent Effect on Acid Hydrolysis of Ethyl Formate

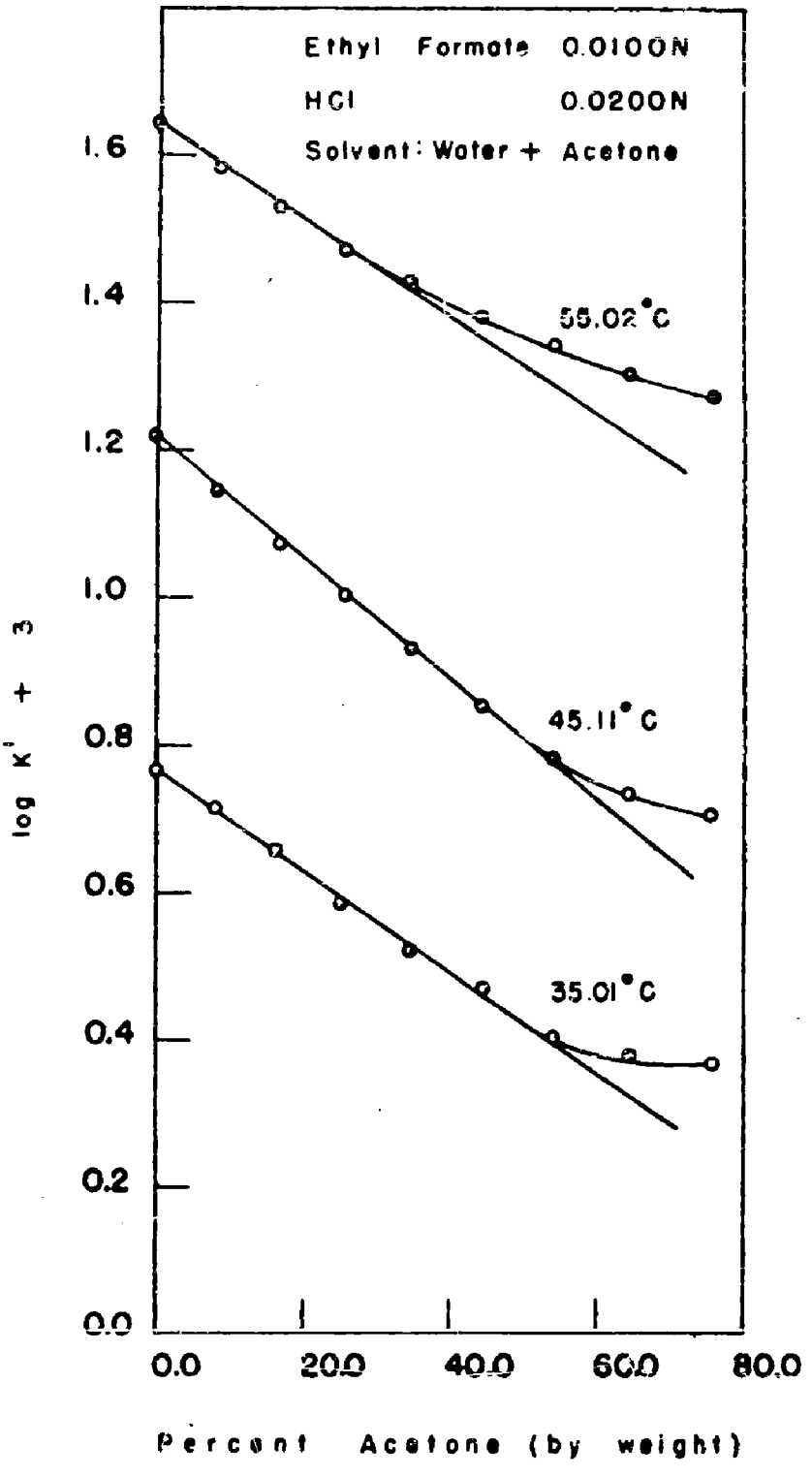


Fig. 2 – Solvent Effect on Acid Hydrolysis of Ethyl Formate

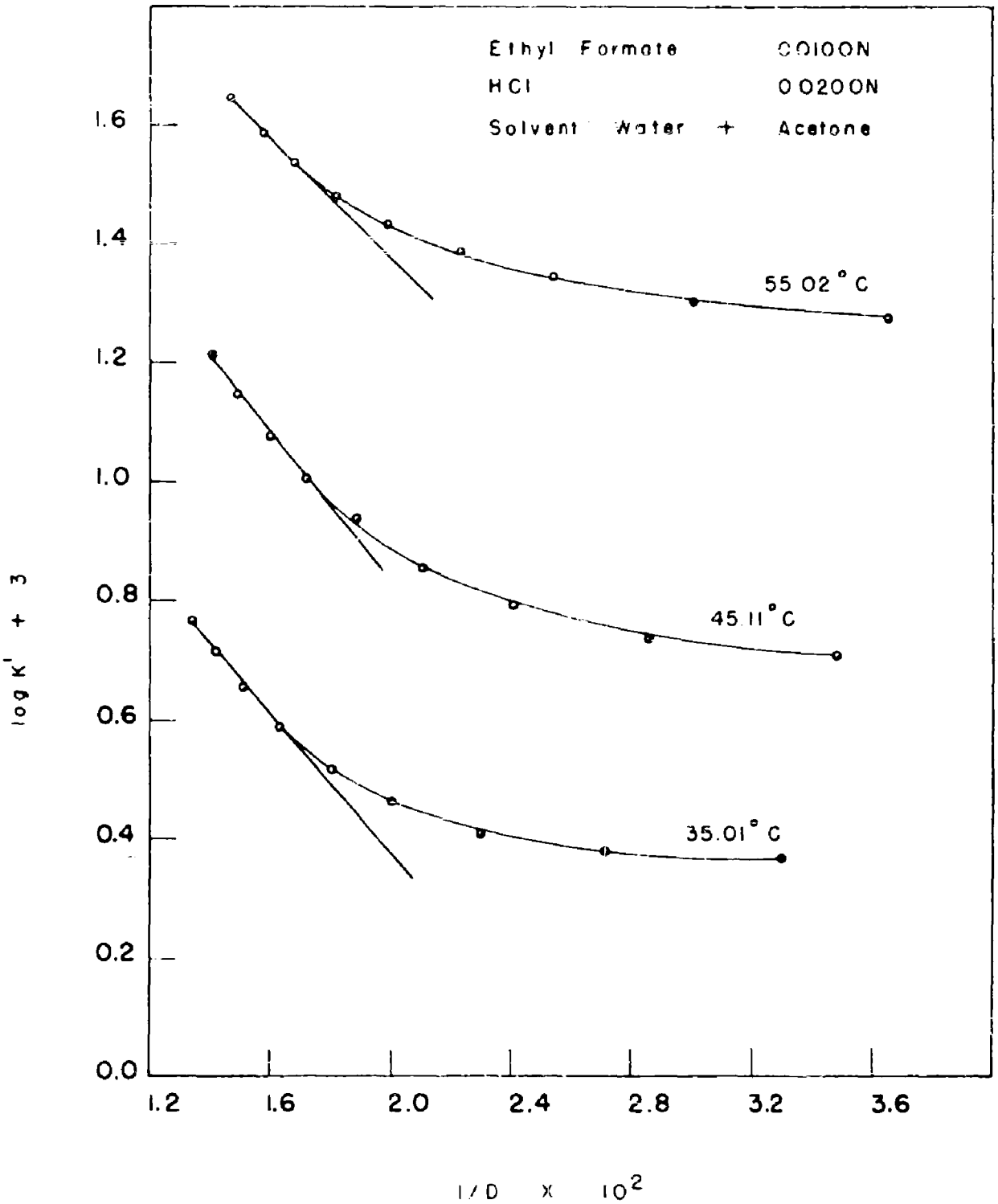


Fig. 3 - Solvent Effect on Acid Hydrolysis of Ethyl Formate

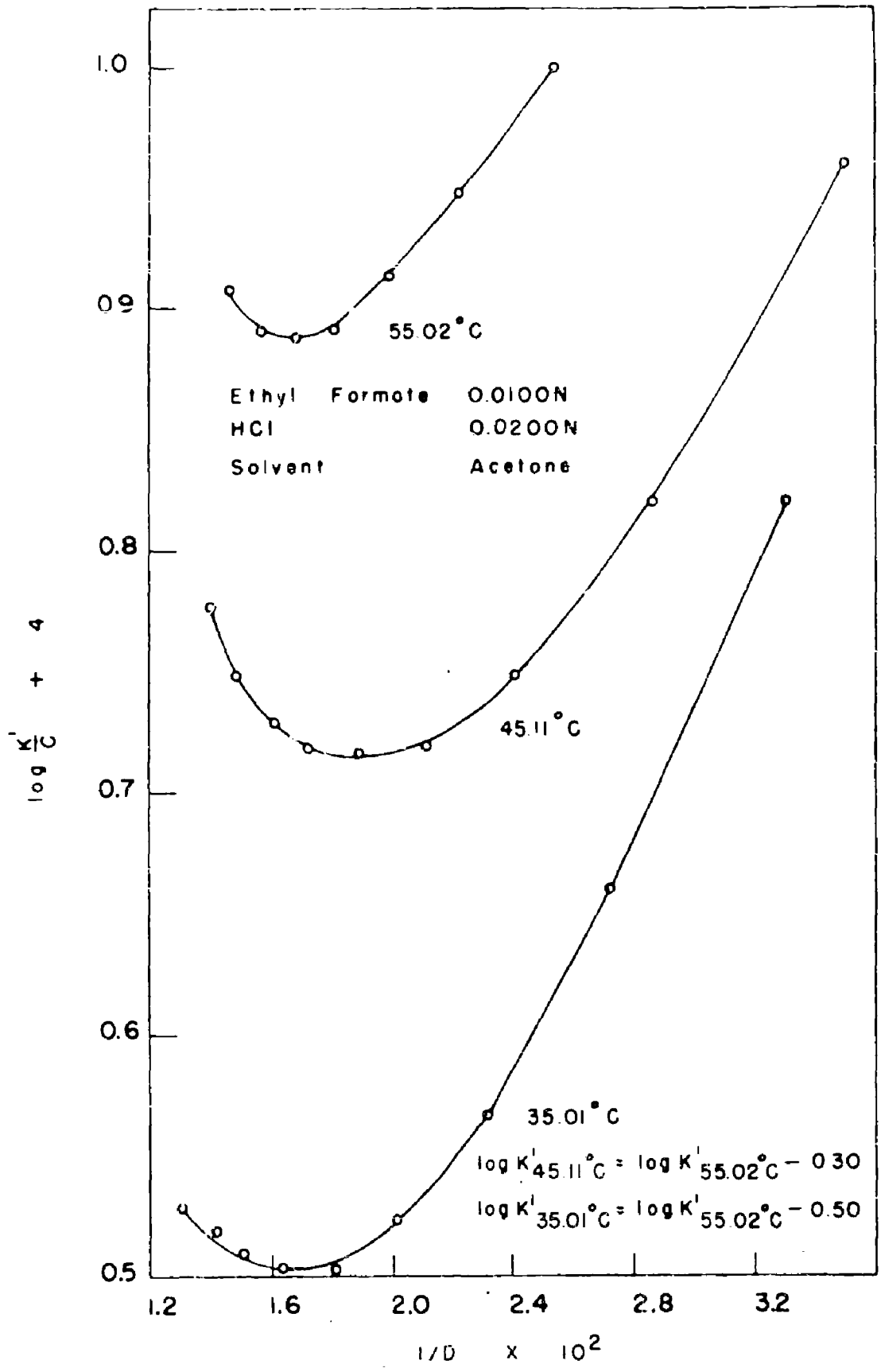


Fig. 4 - Effect of Neutral Salt on Acid Hydrolysis of Ethyl Formate

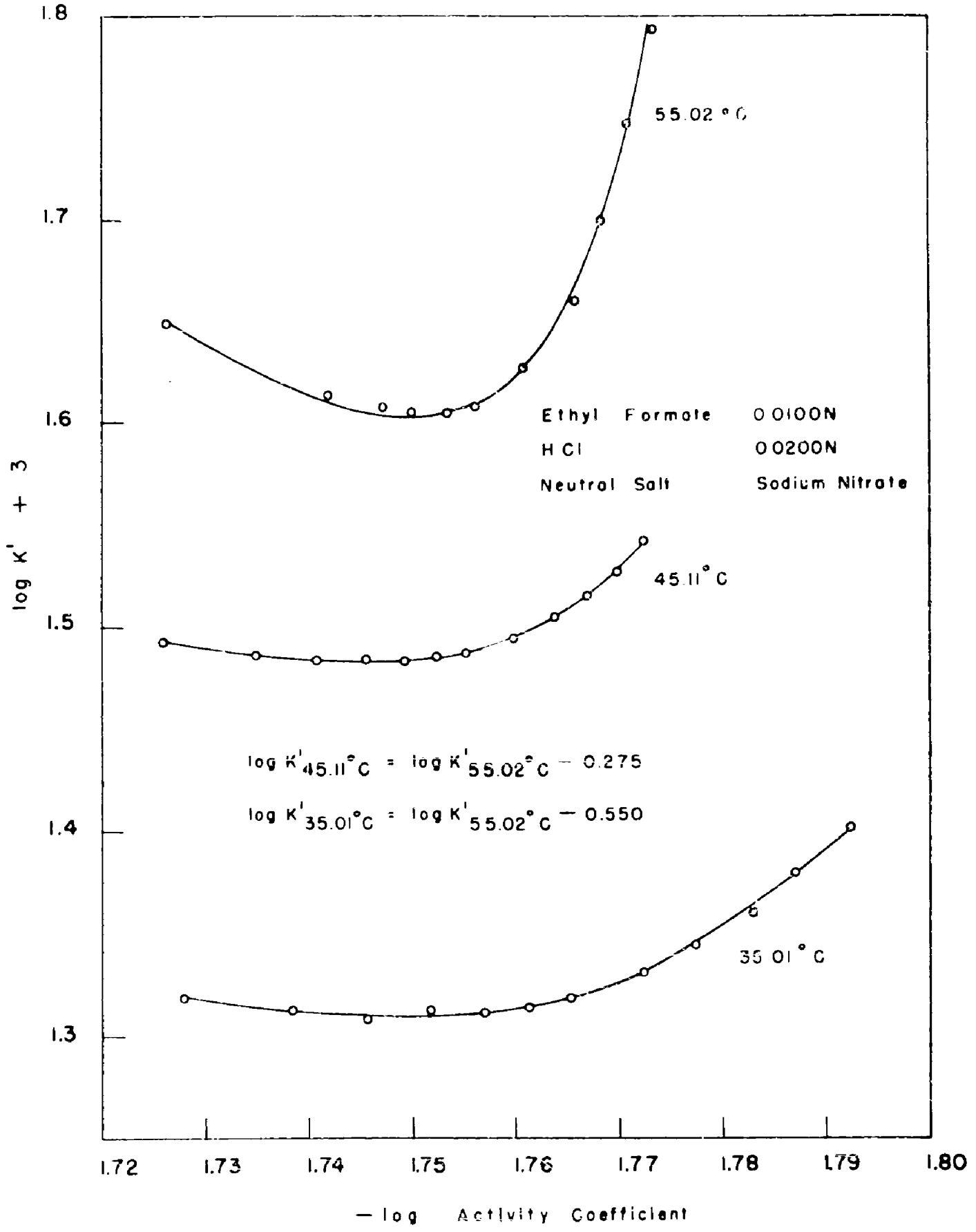
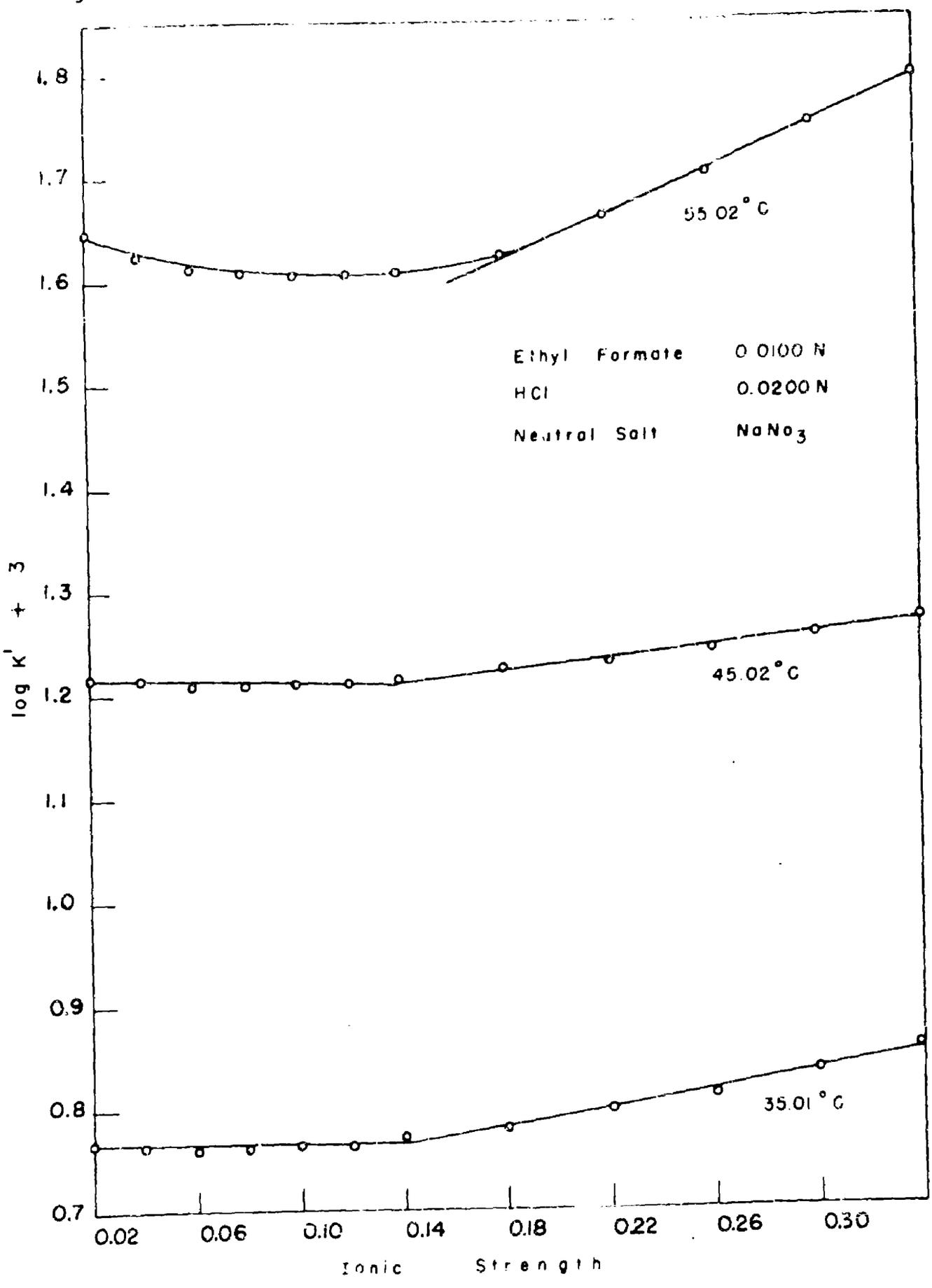


Fig. 5 ~ Effect of Neutral Salt on Acid Hydrolysis of Ethyl Formate



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